Neutron Diffraction Study of Pressure-Dependent Magnetism in Molecule Based Magnets

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Outline

Pressure dependent magnetism
- MBMs and PBAs
- FeCr
- NiCr

FeCr
- Synthesis
- First Principles Calculation
- Elemental analysis
- Structural analysis
- Conclusion

NiCr
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The Big Kahuna!
Pressure Dependent Magnetism

- Magnetostrictive materials
- Villari effect (inverse magnetostrictive effect)
- Device application: sensor, sonar.

Images taken from Wikipedia, NCTE, and Subseaworldnews.com
Molecule Based Magnets (MBMs) & Prussian Blue Analogues (PBAs)

**MBMs**
- Ferromagnetism
- Room-temperature synthesis
- Highly tunable

**PBAs**
- Tunable magnetic ordering
- Mixed valency system
- FCC structure
- Fm$\bar{3}$m (225)
FeCr PBA

- $KFe_3[Cr(CN)_6]_2 \cdot nH_2O$

- Magnetization $\downarrow$: Pressure $\uparrow$

- Hypothesis:
  - Linkage isomerism with spin-crossover (LI)
  - Intrinsic spin-crossover (SC)

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**NiCr PBA**

- $\text{KNI}_3[\text{Cr(CN)}_6]_2 \cdot n\text{H}_2\text{O}$

- **Hypothesis:**
  - LI
  - Random spin-canting
  - Domain wall movement

- **Magnetization ↓:** Pressure ↑

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FeCrx: Synthesis

- $\text{K}_3\text{Cr(CN)}_6$
- $\text{FeCl}_2$
- Cold $\text{D}_2\text{O}$
- No heat
- Dumped together
FeCr: DFT

Variation of FeCr isomers' energy with given lattice

Variation of FeCr isomers' moment with given lattice
FeCr: Elemental Analysis

FT-IR

Linkage isomerization of the cyanide ligand in FeCr

K$\text{Fe}[Cr(CN)\text{6}]_{0.8}$

XPS

K 2p

C 1s

O 1s

N 1s

Cr 2p

Fe 2p
FeCr: XRD

- (2,0,0)
- (2,2,0)
- (2,2,2)
- (4,0,0)
FeCr: Neutron Diffraction
FeCr: Neutron Diffraction
FeCr: Conclusion
**NiCr: Synthesis**

- $K_3Cr(CN)_6$
- $NiCl_2$
- $KCl$
- $D_2O$
- $60 \, ^\circ C$
- Peristaltic Pump
NiCr: DFT

Variation of NiCr isomers' energy with given lattice constant (Å):

- Energy (eV) decreases as the lattice constant increases.
- The energy difference between Ni (C-N) and Ni (N-C) is noticeable.

Variation of NiCr isomers' moment with given lattice constant (Å):

- The Ni moment (µB) increases as the lattice constant increases.
- The moment difference between Ni (C-N) and Ni (N-C) is evident.
NiCr: Elemental Analysis

FT-IR

XPS

$K_{0.42}\text{Ni}[\text{Cr(CN)}_6]_{0.89}$
NiCr: XRD

![Graph showing XRD peaks at (2,0,0), (2,2,0), and (2,2,2)]

<table>
<thead>
<tr>
<th>Element</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
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<tr>
<td>Ni</td>
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<td>0.0000</td>
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<tr>
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<td>0.5000</td>
</tr>
<tr>
<td>C</td>
<td>0.0000</td>
<td>0.2413</td>
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<td>K</td>
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<td>0.2500</td>
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<tr>
<td>N</td>
<td>0.0000</td>
<td>0.0000</td>
<td>1.3490</td>
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</tbody>
</table>
NiCr: Neutron Diffraction
NiCr: Neutron Diffraction
More depolarization at HIGH PRESSURE shows presence of domains effect.
NiCr: Conclusion

LI

Domain wall movement

Random spin-canting
The Big Kahuna!

- No LI in either sample.
- Domain wall movement (NiCr)
- Intrinsic spin-crossover (FeCr)
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Questions?

“The Great Wave off Kanagawa” by Katsushika Hokusai (c. 1829-32)